BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

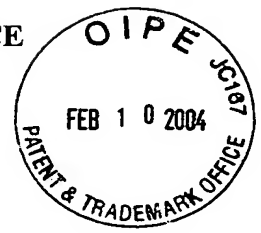
- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

Docket No. 245926US0X DIV

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



IN RE APPLICATION OF: Toshio TSUJIMOTO, et al.

GAU:

SERIAL NO: 10/720,122

EXAMINER:

FILED: November 25, 2003

FOR: SURFACE MODIFICATION PROCESS OF QUARTZ GLASS CRUCIBLE

REQUEST FOR PRIORITY

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

☐ Full benefit of the filing date of U.S. Application Serial Number , filed , is claimed pursuant to the provisions of **35 U.S.C. §120.**

☐ Full benefit of the filing date(s) of U.S. Provisional Application(s) is claimed pursuant to the provisions of **35 U.S.C. §119(e):** **Application No.** **Date Filed**

■ Applicants claim any right to priority from any earlier filed applications to which they may be entitled pursuant to the provisions of **35 U.S.C. §119**, as noted below.

In the matter of the above-identified application for patent, notice is hereby given that the applicants claim as priority:

COUNTRY	APPLICATION NUMBER	MONTH/DAY/YEAR
Japan	2001-318032	October 16, 2001

Certified copies of the corresponding Convention Application(s)

■ are submitted herewith

☐ will be submitted prior to payment of the Final Fee

☐ were filed in prior application Serial No. filed

☐ were submitted to the International Bureau in PCT Application Number
Receipt of the certified copies by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.

☐ (A) Application Serial No.(s) were filed in prior application Serial No. filed ; and

☐ (B) Application Serial No.(s)

- ☐ are submitted herewith
- ☐ will be submitted prior to payment of the Final Fee

Respectfully Submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.

Norman F. Oblon
Registration No. 24,618

Frederick D. Vastine
Registration No. 27,013

Rohith Ravindran
Registration No. 50,385

Customer Number
22850
Tel. (703) 413-3000
Fax. (703) 413-2220
(OSMMN 05/03)

日本国特許庁
JAPAN PATENT OFFICE

別紙添付の書類に記載されている事項は下記の出願書類に記載されている事項と同一であることを証明する。

This is to certify that the annexed is a true copy of the following application as filed with this Office.

出願年月日
Date of Application: ２００１年１０月１６日

出願番号
Application Number: 特願２００１－３１８０３２

[ST. 10/C]: ［ＪＰ２００１－３１８０３２］

出願人
Applicant(s): ジャパンスーパークォーツ株式会社

２００４年　１月２３日

特許庁長官
Commissioner,
Japan Patent Office 今井康夫

出証番号　出証特２００４－３００２０９８

【書類名】　特許願

【整理番号】　MMQ0012

【提出日】　平成13年10月16日

【あて先】　特許庁長官　及川　耕造　殿

【国際特許分類】　B65B 17/00

【発明者】

【住所又は居所】　秋田県秋田市茨島５丁目１４番３号　三菱マテリアルクォーツ株式会社開発センター内

【氏名】　辻　義行

【発明者】

【住所又は居所】　秋田県秋田市茨島５丁目１４番３号　三菱マテリアルクォーツ株式会社開発センター内

【氏名】　辻元　俊夫

【特許出願人】

【識別番号】　592176044

【住所又は居所】　東京都千代田区丸の内一丁目５番１号

【氏名又は名称】　三菱マテリアルクォーツ株式会社

【代理人】

【識別番号】　100088719

【弁理士】

【氏名又は名称】　千葉　博史

【連絡先】　０３－５６１４－８０６１

【手数料の表示】

【予納台帳番号】　070265

【納付金額】　21,000円

【提出物件の目録】

【物件名】　明細書　1

【物件名】　要約書　1

【包括委任状番号】　9723341

【プルーフの要否】　　要

【書類名】　明細書

【発明の名称】　石英ガラスルツボの表面改質方法と表面改質ルツボ

【特許請求の範囲】

【請求項１】　単結晶引上げ用の石英ガラスルツボの表面に、金属有機酸塩または金属炭酸塩とアルコキシシランオリゴマーの部分加水分解物とを含む混合液（以下、シリカゾル液と云う）を付着し、これを焼成してルツボ表面に金属酸化物を含む透明コーティング層を形成することを特徴とする石英ガラスルツボの表面改質方法。

【請求項２】　金属有機酸塩または金属炭酸塩がマグネシウム、カルシウム、ストロンチウム、またはバリウムの何れかの有機酸塩または炭酸塩である請求項１に記載する石英ガラスルツボの表面改質方法。

【請求項３】　石英ガラスルツボ表面の全面または所望の部分にシリカゾル液を塗布して焼成する請求項１または２に記載する石英ガラスルツボの表面改質方法。

【請求項４】　混合液中の金属含有量が酸化物換算で０．５～１５重量％であって珪素濃度がSiO_2換算で０．５～３０重量％のシリカゾル液を用いる請求項１、２または３の何れかに記載する石英ガラスルツボの表面改質方法。

【請求項５】　シリカゾル液をルツボ表面に付着して乾燥した後に、３５０～６００℃で１０～１２０分焼成処理する請求項１～４の何れかに記載する石英ガラスルツボの表面改質方法。

【請求項６】　シリカ質マトリックス中に金属酸化物が分散した透明コーテング層を表面に有する単結晶引き上げ用石英ガラスルツボ。

【請求項７】　請求項１～５の何れか記載の方法で形成された透明コーティング層を有する請求項５に記載する石英ガラスルツボ。

【請求項８】　透明コーティング層に含まれる金属酸化物が結晶化促進剤である請求項６または７に記載する石英ガラスルツボ。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】

本発明は、半導体などに使用するシリコン単結晶を溶融シリコンから引き上げる際に使用する石英ガラスルツボの表面改質方法と表面改質された石英ガラスルツボに関する。

【０００２】

【従来の技術】

シリコン単結晶の引き上げの際にシリコン単結晶に転移が形成される一因として、石英ガラスルツボの内表面に析出したクリストバライトがシリコン融液中に放出されることがあげられる。この対策として、ルツボ内表面に結晶化促進剤を塗布し、ルツボ内表面を早期に結晶化させる方法が知られている（例えば、特許第3054362号、特開平8－2932号など）。これらの方法では、石英ガラスルツボの表面に水酸化バリウム溶液を塗布し、水酸化バリウムと空気中の二酸化炭素と反応して生じた炭酸バリウムをルツボ表面に沈着させ、これを乾燥することによってルツボ表面付着させており、この炭酸バリウムを結晶化促進剤として用いている。

【０００３】

【発明が解決すべき課題】

しかし、従来の表面処理した上記石英ガラスルツボには次のような問題点があり、その解決を求められている。すなわち、（イ）従来の石英ガラスルツボに付着している炭酸バリウム粉はバインダー等によって固着されているのではないために付着力が非常に弱い。このため、製品検査や搬送、収納袋への装入など製造側の作業工程、引き上げ装置のカーボンサセプターに石英ガラスルツボを装着する使用側の作業工程などにおいてルツボ表面の炭酸バリウム粉が剥落しやすく、取り扱い器具や作業員に触れる度に剥がれ落ち、斑になって付着状態が不均一になる。さらに、収納袋を開封する度に炭酸バリウム粉が飛散して作業員の健康を害する惧れがある。（ロ）炭酸バリウム粉が表面に付着しているだけなので付着力が弱く、結晶核になる効率が悪いため炭酸バリウムの付着量が過剰になりやすい。（ハ）洗浄するとルツボ表面に付着させた炭酸バリウム粉が洗い流されるので、炭酸バリウム粉を付着させた後、ルツボ使用までの間、表面に汚れが付いてもルツボを洗浄することができない。

【０００４】

本発明はこのような従来の石英ガラスルツボの課題を解決したものであり、取り扱い器具や作業員に触れても剥落せず、耐久性に優れた透明コーテング層を有する表面改質した石英ガラスルツボとその表面改質方法を提供するものである。

【０００５】

【課題を解決する手段】

すなわち、本発明は、（１）単結晶引上げ用の石英ガラスルツボの表面に、金属有機酸塩または金属炭酸塩とアルコキシシランオリゴマーの部分加水分解物とを含む混合液（シリカゾル液）を付着し、これを焼成してルツボ表面に金属酸化物を含む透明コーティング層を形成することを特徴とする石英ガラスルツボの表面改質方法に関する。

【０００６】

本発明の上記表面改質方法は、（２）金属有機酸塩または金属炭酸塩が、マグネシウム、カルシウム、ストロンチウム、またはバリウムの何れかの有機酸塩または炭酸塩である方法、（３）石英ガラスルツボ表面の全面または所望の部分にシリカゾル液を塗布して焼成する方法、（４）混合液中の金属含有量が酸化物換算で０．５～１５重量％であって珪素濃度がSiO_2換算で０．５～３０重量％のシリカゾル液を用いる方法、（５）シリカゾル液をルツボ表面に付着して乾燥した後に、３５０～６００℃で１０～１２０分焼成処理する方法を含む。

【０００７】

また、本発明は（６）シリカ質マトリックス中に金属酸化物が分散した透明コーテング層を表面に有する単結晶引き上げ用石英ガラスルツボに関する。

本発明の石英ガラスルツボは、（７）上記(1)～(4)の何れか記載の方法で形成された透明コーティング層を有する石英ガラスルツボ、（８）透明コーティング層に含まれる金属酸化物が結晶化促進剤である石英ガラスルツボを含む。

【０００８】

本発明の表面改質石英ルツボは、シリカ質マトリックス中に金属酸化物が分散した硬質で透明なコーテング層がルツボ表面に形成されており、金属酸化物は好ましくは結晶化促進剤として作用する金属種であって、このコーテング層はルツ

ボ表面と一体化しているので極めて安定であり耐久性に優れる。従って器具や作業員に接触した程度では剥離せず、コーテング層に含まれる金属酸化物の付着状態が不均一になる懸念がなく、比較的薄い膜厚のコーテング層でも単結晶引き上げ時にルツボ表面に結晶核が均一に形成されるので、シリコン単結晶の収率を高めることができる。また、従来の炭酸バリウム粉が表面に付着したルツボは酸洗浄によって付着している炭酸バリウム粉が全て洗い流されるので、不純物が含まれていても洗浄することができないが、本発明の表面改質石英ルツボはコーテング工程でルツボに付着した不純物を酸洗浄して除去することができるので、シリコン単結晶への不純物混入を極力防止することができる。

【０００９】

【発明の実施の形態】

以下、本発明を実施形態に基づいて具体的に説明する。

本発明に係る石英ガラスルツボの表面改質方法は、ルツボ表面にシリカ質マトリックス中に金属酸化物が分散した透明コーテング層を形成する方法であり、本発明の石英ガラスルツボはこの透明コーテング層を有するものである。なお、上記金属酸化物はシリカ以外のものであって、好ましくは石英ガラスの結晶化促進剤として作用する金属種であり、具体的には、例えば、マグネシウム、カルシウム、ストロンチウム、バリウム等の酸化物である。

【００１０】

金属酸化物が分散したシリカ質マトリックスからなる透明コーテング層は、金属有機酸塩または金属炭酸塩とアルコキシシランオリゴマーの部分加水分解物とを含む混合液（これをシリカゾル液と云う）を用い、このシリカゾル液をルツボ表面に付着し、これを焼成することによって形成することができる。

【００１１】

透明コーティング層を形成する前駆体液である上記シリカゾル液は、石英ガラスルツボ表面に結晶核の発生を促す結晶化促進剤として有用なマグネシウム、カルシウム、ストロンチウム、バリウム等の金属有機酸塩または金属炭酸塩と、アルコキシシランオリゴマーの部分加水分解物とを必須成分として含有する混合液であり、さらに安定化剤等を含有してもよい。

【００１２】

上記金属の有機酸塩で、最も好ましいのはカルボン酸塩である。カルボン酸塩を形成するアシルオキシ基としては、一般式$C_nH_{2n+1}COO$（ｎは３～７の整数）で表されるものが好適である。具体的には、n－酪酸、α－メチル酪酸、i－吉草酸、2－エチル酪酸、2,2－ジメチル酪酸、3,3－ジメチル酪酸、2,3－ジメチル酪酸、3－メチルペンタン酸、4－メチルペンタン酸、2－エチルペンタン酸、3－エチルペンタン酸、2,2－ジメチルペンタン酸、3,3－ジメチルペンタン酸、2,3－ジメチルペンタン酸、2－エチルヘキサン酸に、3－エチルヘキサン酸等から誘導されるアシルオキシ基が好適に用いられる。

【００１３】

また、2,4－ペンタンジオン(＝アセチルアセトン）、3－メチル－2,4－ペンタンジオン、3－イソプロピル－2,4－ペンタンジオン、2,2－ジメチル－3,5－ヘキサンジオン等のβ･ジケトンを上記カルボン酸塩溶液に混合して使用すると、液の保存安定性が向上する。

【００１４】

これらの有機酸塩は有機溶剤に溶解して使用することが好ましい。好適な有機溶剤としてはエステル及び／又はアルコール、或いは、エステル及び／又はアルコールに更にカルボン酸を混合した混合溶剤を用いることもできる。有機溶剤のエステルとしては、酢酸エチル、酢酸プロピル、酢酸n－プチル、酢酸sec－ブチル、酢酸tert－ブチル、酢酸イソブチル、酢酸n－アミル、酢酸sec－アミル、酢酸tert－アミル、酢酸イソアミルが好ましい。

【００１５】

アルコールとしては、メタノール、エタノール、1－プロパノール、2－プロパノール、1－ブタノール、2－ブタノール、イソープチルアルコール、1－ペンタノール、2－ペンタノール、2－メチル－2－ペンタノール、イソーアミルアルコール等が好適である。アルコール類にはアルコキシアルコール、即ち、エーテル基を含有するアルコールを含む。この種のアルコールの例としては、2－メトキシエタノール、1－メトキシ－21－プロパノールが挙げられる。

【００１６】

他に使用出来る溶媒の例としては、アセトン、メチルエチルケトン、メチルイソブチルケトン等のケトン類、トルエン、キシレン、ヘキサン、シクロヘキサン等の炭化水素類が挙げられる。これらの有機溶剤は２種以上混合して使用してもよい。上記金属のカルボン酸塩を含む溶液は、アルコキシシランオリゴマーの部分加水分解物を含む溶液と所定組成となるように混合して上記シリカゾル液を調製する。このシリカゾル液はルツボ表面に対して高い濡れ性を有し、焼成して脱水すると最終的に有機物が完全に除去されたシリカ質マトリックス中に金属酸化物が分散した硬質透明のシリカ質コーテング被膜を形成する。

【００１７】

本発明に使用するアルコキシシランオリゴマーの部分加水分解物は、アルコキシシランオリゴマーを制御された反応条件で加水分解し、アルコールが離脱した後、生成したＯＨ基どうしが結合してシリカゾルを形成したものであり、好適な出発物質としては、少なくとも１個、好ましくは２個以上、さらに好ましくは３個以上のアルコキシル基を有する任意の１種または２種以上のシラン化合物を使用することができる。具体例としては、テトラエトキシシラン(＝エチルシリケート）、テトラプロボキシシラン、メチルトリエトキシシラン、ジメチルジメトキシシラン、フェニルトリエトキシシラン、クロルトリメチルシラン、各種のシランカップリング剤（例、ビニルトリエトキシシラン、γ－アミノプロピルトリエトキシシラン）などが挙げられる。好ましいのは、最も安価で容易に加水分解するエチルシリケートである。

【００１８】

これらのアルコキシシランは、予め部分的に加水分解させた加水分解物として使用する。この部分加水分解は、酸触媒（例、塩酸などの無機酸、またはp－トルエンスルホン酸などの有機酸）と水の存在下で行われ、この時、酸触媒の使用の有無や使用量、反応系に存在させる加水分解用の水の量、反応温度、反応時間などの反応条件を調節することによって重合度を制御したアルコキシシランオリゴマーの部分加水分解物が得られる。

【００１９】

上記部分加水分解は、水を含有する有機溶媒中で加熱攪拌下で行うことが好ま

しい。反応温度は、好ましくは３０～６０℃、より好ましくは３５～５５℃である。反応時間は２～５時間程度が好ましい。

【００２０】

上記シリカゾル液は、溶液中の金属含有量が酸化物換算で０．５～１５重量％であって珪素濃度がSiO_2換算で０．５～３０重量％となるように、金属有機酸塩含有液または金属炭酸塩含有液とアルコキシシランオリゴマーの部分加水分解物溶液とを混合して調製される。この金属含有量が酸化物換算で０．５重量％未満ではルツボ表面に十分な結晶核を発生させて所望の失透層厚を形成するために重ね塗りが必要になる。一方、この量が１５重量％を上回ると安定な混合液を作り難い。また、珪素濃度がSiO_2換算で０．５重量％未満では形成されたコーテング層の強度が不十分な場合があり、この量が３０重量％を上回ると安定な混合液を作り難いので、珪素濃度は０．５～３０重量％の範囲が好ましい。より好ましい含有量は１～２０重量％である。

【００２１】

上記シリカゾル液をルツボ表面に付着させる方法としてはスプレー法、浸透法などを用いることができ特には制限されない。また、ルツボ表面にシリカゾル液を付着させる範囲も限定されない。ルツボ表面の全体または任意の範囲に付着しても良い。

【００２２】

ルツボ表面にシリカゾル液を付着させた後に焼成を行う。焼成は３５０～６００℃で１０分～１２０分程度が適当である。

【００２３】

【実施例】

〔１〕アルコキシシランオリゴマー部分加水分解物の調製

表１に示した原料の配合比と反応条件で(Ｉ)(II)２種類のアルコキシシランオリゴマーの部分加水分解物を調製した。

〔２〕シリカゾル液の調製

(2-1) 2－エチルヘキサン酸バリウム〔$(C_7H_{15}COO)_2Ba$〕１３．８ｇを、イソアミルアルコール６０ｇと酢酸イソアミル２６．２ｇの混合溶剤に溶解させ

てＢａＯ換算５wt％の液とし、この液２０g、４０g、５０gに、表１(Ｉ)のアルコキシシランオリゴマーの部分加水分解物２０g、５０gを各々添加混合し、さらにＡ液とＢ液は１-ブタノールを加えて濃度調整して、表２のＡ、Ｂ、Ｃに示すシリカゾル液を調製した。

(2-2) 2－エチル酪酸バリウム〔$(C_5H_{11}COO)_2Ba$〕２４.０ｇを、1－ブタノール７０とアセチルアセトン６ｇの混合溶剤に溶解させ、還流してＢａＯ換算１０wt％の液とし、この液２０g、５０gに、表１(II)のアルコキシシランオリゴマーの部分加水分解物４０g、８０gを各々添加混合し、さらにＤ液にはイソアミルアルコールを加えて濃度調整して、表２のＤ、Ｅに示すシリカゾル液を調製した。

(2-3) 表１(Ｉ)のアルコキシシランオリゴマーの部分加水分解物１００gに、平均粒径１０μmの炭酸バリウム粉末０.５gを分散させてシリカゾル液Ｆを調製した。液溜には攪拌羽を装着した装置を用い、炭酸バリウム粉末が沈殿しないように留意した。

【００２４】

〔３〕コーテング層の形成

アーク回転モールド法によって成形した単結晶引上げ用石英ガラスルツボの表面に、表２に示す５種類（Ａ－Ｅ）のシリカソル液をスプレーで塗布し、５００℃で３０分焼成してコーテング膜を形成した。また、溶液Ｆ、Ｈを用いて上記石英ガラスルツボを表面処理した。試料No.６はシリカゾル液Ｆを用い、これをルツボ表面にスプレーで塗布し、６００℃で３０分焼成したものである。試料No.８は水1ﾘｯﾄﾙに３gの割合で水酸化バリウム八水和物を混合した溶液Ｈを用い、これを３００℃に加熱したルツボに炭酸ガスで噴きつけたものである。

【００２５】

〔４〕コーテング膜の強度

表２に示す溶液（Ａ、Ｆ、Ｈ）を用いて形成したコーテング膜の機械的強度を規格（JIS 5600-5-4）に従って評価した。鉛筆は市販品（商品名：三菱ユニ）を用い、手掻き法で実施した。その結果を表３に示した。本発明に係るＡ溶液によって形成したコーテング膜はガラス質であるので、鉛筆で傷を付けることは不可能

であった。また溶液Ｆを用いたものは炭酸バリウム粉末を含むがシリカ成分がバインダーとなっているため、鉛筆で傷をつけることは不可能であった。一方、従来の溶液Ｈによって形成したコーテング膜は硬度６Ｈの鉛筆で引っ掻き傷がついた。この結果から本発明のコーティング膜は従来のものより格段に強い機械的性質を有することがわかった。

【００２６】

〔５〕洗浄試験

表２に示すコーティング処理した石英ガラスルツボ（No.１、No.６、No.８）の洗浄試験を行った。試験は、(1)純水洗浄した後に乾燥、(2)希塩酸で洗浄した後に純水で洗浄して乾燥の各工程について行った。各洗浄試験後に表面に残ったバリウムの付着量を表３に示した。本発明の石英ルツボ(No１)は水洗工程(1)および酸水洗(2)の何れにおいてもバリウムが除去されず、付着量が変わらなかった。また本発明の石英ルツボ(No.６)はバリウムの形態が従来品と同じ炭酸ナトリウムであるが、シリカゾル液に分散して塗布し、焼成したので、形成されたシリカ皮膜が保護膜の役割を果たしており、上記石英ルツボ(No.１)と同様に水洗工程(1)および酸水洗(2)の何れにおいてもバリウムが除去されなかった。一方、従来品(No.８)は炭酸バリウムが表面に付着しているだけなので、水洗工程(1)でバリウムが若干洗い流され、酸水洗工程(2)においては炭酸バリウムが完全に洗い流された。

【００２７】

〔６〕単結晶化率試験

上記透明コーティング層を形成した石英ガラスルツボ〈No.1～No.5）、上記アルコキシシランオリゴマーの部分加水分解物に炭酸バリウム粉末を分散したもの（No.6）を用いてシリコン単結晶引上げ試験を行った。この単結晶化率（シリコン単結晶収率）を表４に示した。また、比較のため、表面改質処理を行わず結晶化層を形成しない石英ガラスルツボ（No.7）、および上記従来の方法で結晶化層を形成した石英ガラスルツボ（No.8）についても同様の引上げ試験を行った。この単結晶化率を表４に示す。また、引上げ後のルツボの結晶化層を測定した。結晶化層厚を表４に示す。表４の結果に示すように、本発明例の石英ガラスルツボ

は、比較的少量のバリウムでも十分な層厚の結晶化層がルツボ表面に形成されており、高い単結晶化率が達成される。一方、比較例No.７は単結晶化率が大幅に低く、また従来の方法で炭酸バリウムを付着したもの（No.8）は、本発明例とほぼ同じバリウム付着量の場合に引上げ後のルツボには結晶化層が認められず、また単結晶化率も大幅に低かった。

【００２８】

〔７〕その他の結晶化促進剤

Ｍｇ、Ｃａ、Ｓｒの２-エチルヘキサン酸塩を表１（Ｉ）のアルコキシシランオリゴマーの部分加水分解物に添加してシリカゾル液を調製した。これを１０cm角の石英片にスプレーで塗布し、５００℃で３０分間焼成し、透明なコーティング膜を得た。金属付着量（酸化物換算）は何れも１μg/cm^{2}になるように調整した。これを電気炉に入れ、アルゴンガス１気圧下、１４５０℃で５時間焼成した。上記何れの金属を使用しても均一な結晶化層が得られることを確認した。

【００２９】

【表１】

	オリゴマー(I)	オリゴマー(II)
出発原料・使用量	エチルシリケート40　１５０ｇ	エチルシリケート40　６７.５ｇ
溶剤・使用量	エチルアルコール　４００ｇ	エチルアルコール　1.1ｇ
触媒・使用量	６０%濃度硝酸　0.6ｇ	６０%濃度硝酸　0.7ｇ
水添加量	４５ｇ	３６.４ｇ
反応温度・時間	４５℃・３時間	４５℃・３時間
シリカ固形分	約１０wt%	約２５wt%

【００３０】

【表２】

No	シリカゾル液						金属酸化物付着量
	種類	オリゴマー	金属塩含有液	希釈アルコール	BaO量	SiO_2量	
1	A	(I) 20g	BaO換算5wt% 20g	ブタノール 60g	1	2	0.6
2	B	(I) 20g	BaO換算5wt% 40g	ブタノール 40g	2	2	0.8
3	C	(I) 5g	BaO換算10w% 50g	−	5	5	0.9
4	D	(II) 40g	BaO換算10wt% 50g	イソアミル 10g	5	10	5.2
5	E	(II) 80g	BaO換算10wt% 20g	−	2	20	9.5
6	F	(I) 100g	炭酸Ba粉末 0.5g	−	0.1	10	2.1
7	G	表面処理なし					0
8	H	従来の炭酸Ba粉末					0.9

(注) オリゴマーの(I)(II)は表１と同じ、BaOおよびSiO_2の量はwt%
イソアミルはイソアミルアルコール、金属酸化物付着量は$\mu g/cm^2$

【００３１】

【表３】

試料No.	1	6	8
シリカゾル液	A	F	H
被膜硬度（鉛筆硬度）	６Ｈで無傷	６Ｈで無傷	６Ｈで傷発生
洗浄処理後の金属付着量			
未処理	0.6	2.1	0.9
(1)水洗後、乾燥	0.6	2.1	0.8
(2)酸洗浄後、水洗、乾燥	0.6	2.1	0

(注) 金属付着量は$\mu g/cm^2$

【００３２】

【表４】

No	1	2	3	4	5	6	7	8
単結晶化率%	73	75	77	75	71	73	35	40
引き上げ後の結晶化層μm	80	77	83	95	90	103	0	0

【００３３】

【発明の効果】

本発明の石英ガラスルツボは表面に結晶化促進剤を含む透明コーティング層を有し、この透明コーテング層はルツボと一体に形成されているので剥離することがなく、コーテング層に含まれるバリウム等の結晶化促進剤の付着状態が均一に維持される。このため単結晶引き上げ時に、ルツボ表面に結晶核が均一に形成され高い単結晶化率を達成することができる。また、ルツボ製造後の検査から出荷に至る作業工程やルツボ使用側の作業工程において、取り扱い器具や作業員との接触によって剥がれ落ちる心配が無く、従来のようなルツボを収納した袋を開封するたびに炭酸バリウム微粉が飛散する問題がない。

【書類名】　要約書

【要約】

【課題】　ルツボ表面の結晶化促進剤を含む透明コーテング層を有する表面改質石英ガラスルツボと表面改質方法を提供する。

【解決手段】　石英ガラスルツボの表面に、金属有機酸塩とアルコキシシランオリゴマーの部分加水分解物とを含む混合液を付着して焼成し、シリカ質マトリックス中に金属酸化物が分散した透明コーテング層を表面に有する単結晶引き上げ用石英ガラスルツボを得る。

【選択図】　なし

特願２００１－３１８０３２

出　願　人　履　歴　情　報

識別番号　［５９２１７６０４４］

１．変更年月日　１９９２年　７月２１日
［変更理由］　新規登録
住　所　東京都千代田区丸の内１丁目５番１号
氏　名　三菱マテリアルクォーツ株式会社

２．変更年月日　２００２年　５月２２日
［変更理由］　名称変更
住　所　東京都千代田区丸の内１丁目５番１号
氏　名　ジャパンスーパークォーツ株式会社

Application No. : 2001-318032

DECLARATION

I, NORIBUMI KIKUCHI, a subject of Japan residing at c/o IP Service Corporation, Oguma Bldg., 2-10, Miya-cho, Saitama-shi, Saitama-ken 330-0802, Japan, solemnly and sincerely declare:

That I have thorough knowledge of Japanese and English languages; and

That the attached pages contain a correct translation into English of the priority certificate of the following Japanese Patent Application:

APPLICATION NUMBER	DATE OF APPLICATION
2001-318032	16 October 2001

Singed this 11 th day of October, 2002

Noribumi Kikuchi

NORIBUMI KIKUCHI

Application No. : 2001-318032

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this office.

Date of application: 16 October 2001

Application Number: Patent Application 2001-318032

Applicant (s) : Japan Super Quartz Co., Ltd

27 September 2002

Commissioner, Japan Patent Office SHINICHIRO OHTA

Application No. : 2001-318032

[Name of Document] Request for Patent

[Reference No.] MMQ0012 (Application No. : 2001-318032)

[File Date] 16 October 2001

[Address] Commissioner, Japan Patent Office

Mr. Oikawa Kouzou

[Int. Cl.] B65B 17/00

[Inventor]

[Address or Residence] C/O Mitsubishi Material Quartz Co. Ltd, R&D Center, 5-14-3, Barajima, Akita-shi, Akita-ken, Japan

[Name] Tsuji Yoshiyuki

[Inventor]

[Address or Residence] C/O Mitsubishi Material Quartz Co. Ltd, R&D Center, 5-14-3, Barajiima, Akita-shi, Akita-ken, Japan

[Name] Tsujimoto Toshio

[Applicant for Patent]

[Identification No.] 592176044

[Address or Residence] 1-5-1, Marunouchi, Chiyoda-ku, Tokyo, Japan

[Name] Mitsubishi Material Quartz Co. ltd.

[Agent]

[Identification No.] 100088719

[Patent Attorney]

[Name] Chiba Hiroshi

[Where to make contact] 03-5614-8061

[Indication of Commission]

[Number of deposit account] 070265

[Amount of Payment] 21,000 yen

[List of Documents Attached]

[Name of Document] Specification 1

[Name of Document] Abstract 1

[No. of General Power of Attorney] 9723341

[Proof] Required

[Name of Document] Specification

[Title of the Invention]

Surface modification process of quartz glass crucible and surface modified crucible

[CLAIM]

What is claimed is

[Claim 1] A surface modification process of a quartz glass crucible, said process comprising,

coating a mixed solution containing a metal organic acid salt or a metal carbonate and a partial hydrolyzate of an alkoxysilane oligomer, (hereafter referred to as the silica sol liquid), on the surface of the quartz glass crucible for pulling up silicon single crystal, and

baking said crucible coated with said silica sol liquid to form a transparent coated layer comprising a metal oxide on said surface of the crucible.

[Claim 2] The surface modification process of the quartz glass crucible according to Claim 1,

wherein the metal organic acid salt or the metal carbonate is a metal organic acid salt or a metal carbonate of any one of magnesium, calcium, strontium, or barium.

[Claim 3] The surface modification process of the quartz glass crucible according to Claim 1 or Claim 2,

wherein the silica sol liquid is coated on the whole or the desired part of the surface of the quartz glass crucible to be baked.

[Claim 4] The surface modification process of the quartz glass

crucible according to Claim 1, Claim 2, or Claim 3,

wherein the silica sol liquid comprises 0.01 to 15 weights % of metal content in the mixed solution, which is calculated as an oxide, and 0.5 to 30 weights % of silicon concentration, which is calculated as SiO_2.

[Claim 5] The surface modification process of the quartz glass crucible according to any one of from Claim 1 to Claim 4, the process further comprising,

coating the silica sol liquid on the surface of the crucible to be dried, and baking said dried silica sol liquid at a temperature 350 to 600℃ for 10 to 120 minutes.

[Claim 6] A quartz glass crucible for pulling up silicon single crystal, comprising a transparent coated layer on the surface of said crucible, wherein said coated layer comprises a metal oxide dispersed in a silica matrix.

[Claim 7] The quartz glass crucible according to Claim 5,

comprising the transparent coated layer formed by the process according to any one of from Claim 1 to Claim 5.

[Claim 8] The quartz glass crucible according to Claim 6 or Claim 7, wherein the metal oxide in the transparent coated layer is a crystallization promoter.

[0001]

[BACKGROUND OF THE INVENTION]

[Field of the Invention]

The present invention relates to a surface modified quartz glass

crucible and its modification process, in which the crucible is used in the process of pulling up silicon single crystal used for a semiconductor, etc., from molten silicon.

[0002]

[Discussion of the Background]

As one of the causes that a dislocation is formed in silicon single crystal in the pulling method, it has been known that cristobalite formed on the inside surface of the quartz glass crucible is released into the molten silicon. As a counter measure to this problem, it is also known that a process, in which a crystallization promoter is coated on the inside surface of the crucible to crystallize the inside surface of the crucible at an early stage of pulling up. (e.g. U.S. PAT. No. 5,976,247, Japanese Pat. No. 3,100,836) In these inventions, a barium hydroxide solution is coated on the surface of the quartz glass crucible, and the coated barium hydroxide reacts with carbon dioxide in air to form barium carbonate on the surface of the crucible. The barium carbonate is adhered on the surface of the crucible by drying it and is used as the crystallization promoter.

[0003]

[Problems to be solved]

However, there are the following problems in said quartz glass crucible, which is surface treated by the conventional methods, and solving them is required. That is, (A) since the barium carbonate powder adhered on the quartz glass crucible by the conventional methods is not fixed with any

binder, the adhesion strength of the powder is very weak. Therefore, the barium carbonate powder on the surface of the crucible is easily abraded and fallen off when contacted with the handling instruments and the persons. Such abrasion occurs in the production process of the crucibles, such as product inspection, conveyance, and insertion to a carrying case, etc. It also occurs in the user's process, in which the quartz glass crucible is set on the carbon susceptor in the crystal puller. As a result, its adhesion state becomes to non-uniform spot-like. Furthermore, there is also a possibility that worker health is negatively affected because the barium carbonate powder is scattered when the carrying case is opened. (B) Since the barium carbonate powder is only adhered on the surface, the adhesion strength of powder is very weak and the nucleation efficiency of the crystal is low, and so that the adhesion amount of barium carbonate becomes easily excessive. (C) If the crucible is washed, the barium carbonate powder adhered on the surface of the crucible is washed away. It is then impossible to wash the crucible after the adhesion of the barium carbonate powder to the use of the crucible, even if some contaminants adhere on the surface of the crucible.

[0004]

The present invention solves these problems of the conventional quartz glass crucible and provides the surface modified quartz glass crucible having a transparent coated layer, which is not abraded when contacted with the handling instruments or the persons and has sufficient durability, and also provides its surface modification process.

[0005]

[Means to be solved]

That is, the present invention relates to the following surface modification process of the quartz glass crucible.

[1] A surface modification process of a quartz glass crucible, the process comprising,

coating a silica sol liquid comprising a metal organic acid salt or a metal carbonate and a partial hydrolyzate of an alkoxysilane oligomer, on the surface of the quartz glass crucible for pulling up silicon single crystal, and baking said crucible coated with said silica sol liquid to form a transparent coated layer comprising a metal oxide on said surface of the crucible.

[0006]

In addition, said surface modification process of the present invention includes the following processes.

[2] The surface modification process of the quartz glass crucible, wherein the metal organic acid salt or the metal carbonate is a metal organic acid salt or a metal carbonate of any one of magnesium, calcium, strontium, or barium.

[3] The surface modification process of the quartz glass crucible, wherein the silica sol liquid is coated on the whole or the desired part of the surface of the quartz glass crucible to be baked.

[4] The surface modification process of the quartz glass crucible, wherein the silica sol liquid comprises from 0.01 to 15 weights % of metal content in the mixed solution, which is calculated as an oxide, and from 0.5

to 30 weights % of silicon concentration, which is calculated as SiO_2.

[5] The surface modification process of the quartz glass crucible, further comprising,

coating the coated silica sol liquid on the surface of the crucible to be dried, and

baking said dried silica sol liquid at a temperature from 350 to 600℃ for 10 to 120 minutes.

[0007]

Moreover, the present invention also relates to the following quartz glass crucible.

[6] A quartz glass crucible for pulling up silicon single crystal,

comprising a transparent coated layer on the surface of said crucible, wherein said coated layer comprises a metal oxide dispersed in a silica matrix

In addition, the quartz glass crucible of the present invention includes the following crucibles.

[7] The quartz glass crucible,

comprising the transparent coated layer formed by the process according to any one of from said [1] to [4].

[8] The quartz glass crucible,

wherein the metal oxide in the transparent coated layer is a crystallization promoter.

[0008]

The surface modified quartz glass crucible of the present invention has a hard and transparent coated layer, in which the metal oxide is dispersed in a silica matrix, on the surface of the crucible, and it is preferable that the metal oxide comprises a metal which acts as the crystallization promoter. In addition, since said coated layer becomes to the integrated structure to the surface of the crucible, it is very stable and has high durability. Therefore, there is no abrasion when only contacted with the instruments or the persons, and no problem that the adhesion state of the metal oxide in the coated layer becomes to non-uniform. In addition, even if the coated layer is comparatively thin, the surface of the crucible is crystallized uniformly during pulling up the single crystal, and so that a dislocation free ratio of silicon can be increased. Moreover, regarding the conventional quartz glass crucible having the adhered barium carbonate powder on its surface, since all barium carbonate powder is washed away by the acid washing, it is impossible to wash the crucible even if some contaminants are contained. However, regarding the surface modified quartz glass crucible of the present invention, since contaminants adhered on the crucible in the coating process can be removed by acid washing, the mixing of the contaminants to the silicon single crystal can be prevented as much as possible.

[0009]

[DETAILED DESCRIPTION OF THE PREFERED EMBODIMENTS]

Hereafter, the present invention is explained concretely according to

the preferred embodiment.

The surface modification process for producing the quartz glass crucible of the present invention is a formation process of the transparent coated layer on the surface of the crucible, in which the metal oxide is dispersed in the silica matrix. Moreover, the quartz glass crucible of the present invention has said transparent coated layer. In addition, said metal oxide comprises a metal except for silicon, and it is preferable that said metal acts as the crystallization promoter of the quartz glass. Concretely, the metal is for example, magnesium, calcium, strontium, or barium etc.

[0010]

The transparent coated layer, in which the metal oxide is dispersed in the silica matrix, can be formed by coating the mixed solution (the silica sol liquid) containing the metal organic acid salt or the metal carbonate and the partial hydrolyzate of alkoxysilane oligomer on the surface of the crucible, and by baking this coated silica sol liquid.

[0011]

Said silica sol liquid, which is a precursor liquid forming the transparent coated layer, is the mixed solution which contains the metal organic acid salt or the metal carbonate and the partial hydrolyzate of an alkoxysilane oligomer as an indispensable components. The metal organic acid salt or the metal carbonate is for example a salt of magnesium, calcium, strontium, or barium, which is useful metal as the crystallization promoter to promote the formation of the cristobalte layer on the surface of the quartz

glass crucible. In addition, it is available that said silica sol liquid also contains a stabilizing reagent.

[0012]

The most preferable one in said metal organic acid salts is carboxylate. As an acyloxy group to form the carboxylate, the materials indicated by the general formula $C_nH_{2n+1}COO$, in which n is integer of 3 to 7, are preferable. Concretely, the acyloxy group derived from n-butyric acid, α-methyl butyric acid, iso-valeric acid, 2-ethyl butyric acid, 2,2-dimethyl butyric acid, 3,3-dimethyl butyric acid, 2,3-dimethyl butyric acid, 3-methyl pentanoic acid, 4-methyl pentanoic acid, 2-ethyl pentanoic acid, 3-ethyl pentanoic acid, 2,2-dimethyl pentanoic acid, 3,3-dimethyl pentanoic acid, 2,3-dimethyl pentanoic acid, 2-ethyl hexanoic acid, or 3-ethyl hexanoic acid, etc., can be used suitably.

[0013]

Moreover, when a β-diketone, such as 2,4-pentanedione (= acetylacetone), 3-methyl-2,4-pentanedione, 3-isopropyl-2,4-pentanedione, or 2,2-dimethyl-3,5-hexanedion etc., is mixed with said carboxylate solution, the preservation stability of the liquid is improved.

[0014]

It is preferable that these organic acid salts are dissolved in an organic solvent. As the suitable organic solvent, an ester and / or an alcohol, or the mixed solvent, in which the carboxylic acid is further mixed with an

ester and / or an alcohol, can be used. As the ester of the organic solvent, ethyl acetate, propyl acetate, n-butyl acetate, sec-butyl acetate, tert-butyl acetate, iso-butyl acetate, n-amyl acetate, sec-amyl acetate, tert-amyl acetate, and iso-amyl acetate, are preferable.

[0015]

As an alcohol, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, iso-butyl alcohol, 1-pentanol, 2-pentanol, 2-methyl-2-pentanol, and iso-amyl alcohol, etc., are suitable. In alcohols, an alkoxy alcohol, i.e., the alcohol containing an ether group, is included. For example, 2-methoxyethanol and 1-methoxy-2-propanol can be used.

[0016]

As the other example of a usable solvent, a ketone, such as acetone, methylethylketone, and methylisobutylketone, and a hydrocarbon, such as toluene, xylene, hexane, and cyclohexane, can be used. It is possible that a mixture of two or more kinds of these organic solvents is used. The solution containing a carboxylate of a metal is mixed with the solution containing the partial hydrolyzate of alkoxysilane oligomer, to provide the predetermined composition, and the silica sol liquid is prepared. The silica sol liquid has high wettability to the surface of the crucible. The final hard and transparent silica coated layer, in which the metal oxide is dispersed in the silica matrix, can be formed by baking to dehydrate said silica sol liquid after the organic components are removed completely.

[0017]

The partial hydrolyzate of alkoxysilane oligomer used in the present invention is obtained by the process in which alkoxysilane oligomer is hydrolyzed under the controlled reaction condition, and after the alcohol is removed, each generated OH group is bonded together to form the silica sol. As the suitable starting material, one or more silane compounds having at least one, preferably more than two, and more preferably more than three alkoxyl groups, can be used. Concretely, tetraethoxysilane (= ethylsilicate), tetrapropoxysilane, methyltriethoxysilane, dimethylmethoxysilane, phenyltriethoxysilane, chlorotrimethylsilane, various kinds of silane coupling reagents, such as vinyltriethoxysilane, γ-aminopropyltriethoxysilane, etc., can be mentioned. Ethylsilicate, which is the cheapest and to be easily hydrolyzed, is preferred.

[0018]

These alkoxysilanes are used as the hydrolyzate, which is partially hydrolyzed beforehand. Said partial hydrolysis is carried out in the presence of an acid catalyst, i.e., an inorganic acid, such as hydrochloric acid, or an organic acid, such as p-toluenesulfonic acid, and water. Then, the reaction conditions, including, whether using the acid catalyst or not, the amount of acid catalyst, the amount of the water for hydrolysis in the reaction system, the reaction temperature and the reaction time, are adjusted to obtain the partial hydrolyzate of alkoxysilane oligomer, in which the degree of polymerization is controlled.

[0019]

It is preferable that said partial hydrolysis is carried out with heating and stirring in an organic solvent containing water. In addition, it is preferable that the reaction temperature is 30 to 60℃, more preferably 35 to 55℃, and the reaction time is 2 to 5 hours.

[0020]

Regarding said silica sol liquid, the metal organic acid salt or the metal carbonate and the partial hydrolyzate of an alkoxysilane oligomer are mixed and prepared, and so that the amount of metal content becomes 0.5 to 10 weight %, which is calculated as an oxide, and the silicon concentration becomes 0.5 to 30 weight %, which is calculated SiO_2. When the metal content is less than 0.5 weight %, which is calculated as an oxide, a repeat coating is necessary to form the desired devitrification layer thickness on the surface of the crucible. On the other hand, when the content is more than 15 weight %, it is difficult to make a stable mixed solution. Moreover, when the silicon concentration is less than 0.5 weight %, which is calculated as SiO_2, the strength of the formed coated layer is not sufficient, and when said concentration is more than 30 weight %, it is difficult to make the stable mixed solution. It is preferable that the silicon concentration is 0.5 to 30 weight %, more preferably 1 to 20 weight %.

[0021]

As the method for coating said silica sol liquid on the surface of the crucible, a spray method and a dipping method, etc. can be used, and the

coating method is not limited. In addition, the area, in which the silica sol liquid is coated on the surface of the crucible, is not also limited. Moreover, it is available that said silica sol liquid is coated on the whole or an arbitrary area of the surface of the crucible.

[0022]

The silica sol liquid is coated on the surface of the crucible and is baked. It is suitable that the baking temperature is 350 to 600℃, and the baking time is 10 to 120 minutes.

[0023]

[EXAMPLE 1]

Preparation of a partial hydrolyzate of alkoxysilane oligomer

Two kinds of a partial hydrolyzate of alkoxysilane oligomer of (Ⅰ) and (Ⅱ) were prepared at the mixing ratios of raw materials and the reaction conditions, which were shown in Table 1.

[EXAMPLE 2]

Preparation of the silica sol liquid

(2-1) 13.8g of 2-ethylhexanoic barium $(C_7H_{15}COO)_2Ba$ was dissolved in a mixed solvent of 60g of iso-amyl alcohol and 26.2g of iso-amyl acetate to make 5 weight % solution, which was calculated as BaO. Next, 20g and 50g of partial hydrolyzates of alkoxysilane oligomer shown in Table 1 (Ⅰ), were added and mixed with 20g, 40g, and 50g of said solutions respectively. Furthermore, in the liquid A and the liquid B, 1-butanol was added to adjust

the concentrations. Then, the silica sol liquids of A, B, and C shown in Table 2 were prepared.

(2-2) 24.0g of 2-ethylbutyric barium $(C_5H_{11}COO)_2Ba$ was dissolved in a mixed solvent of 70g of 1-butanol and 6g of acetylacetone, and refluxed to make 10 weight % solution, which were calculated as BaO. Next, 40g and 80g of the partial hydrolyzates of alkoxysilane oligomer shown in Table 1 (II) were added to mix with 20g and 50g of said solutions respectively. Furthermore, in the liquid D, iso-amyl alcohol was added to adjust the concentration. Then, the silica sol liquids D and E shown in Table 2 were prepared.

(2-3) 0.5g of barium carbonate powder having an average particle size of 10μm was dispersed in 100g of the partial hydrolyzate of alkoxysilane oligomer shown in Table 1 (I) to prepare the silica sol liquid F in Table 2. In the reaction vessel for the preparation, the equipment having the stirring propeller was used to prevent the precipitation of the barium carbonate powder.

[0024]

[EXAMPLE 3]

Formation of the coated layer

Five kinds of the silica sol liquids, (A-E), which were shown in Table 2, were sprayed to coat the surface of the quartz glass crucibles for silicon single crystal production, and the coated layers were formed by baking the coated liquids at 850℃ for 30 minutes, wherein the crucibles were made by an arc fusion with rotating mold method and generally used in the process

to produce the crucible for pulling up a single crystal. In addition, said quartz glass crucibles were surface treated by using the liquids F and H. Sample No.6 was made by spaying the silica sol liquid F to coat the surface of the crucible to be baked at 850℃ for 30 minutes. In addition, Sample No.8 was made by a conventional coating method. That is, the liquid H, in which barium hydroxide octahydrate was mixed with water, where the mixing ratio is 3g of barium hydroxide octahydrate in 1l of water, was sprayed on the crucible to heat at 300℃ with carbon dioxide gas.

[0025]

[EXAMPLE 4]

Strength of the coated layer

The mechanical strength of the coated layer formed by using the liquids A, F, and H, which were shown in Table 2, was evaluated according to the specification standard (JIS 5600-5-4). This evaluation was carried out by a scratching method using the marketed pencil (the trade name was Mitsubishi UNI). The results were shown in Table 3. Regarding the coated layer formed by using the liquid A of the present invention, since the layer was glassy, it is impossible to give a scratching with the pencil. Moreover, regarding the coated layer formed by using the liquid F, although the barium carbonate powder was contained, the silica component became a binder, and so that it is impossible to give the scratching with the pencil. On the other hand, regarding the coated layer formed by using the conventional liquid H, the scratching is given by using a pencil of 6H hardness. From these results, it was confirmed that the coated layer of the present invention

had remarkable stronger mechanical property than the conventional layer.

[0026]

[EXAMPLE 5]

Washing test

Washing tests were carried out on the quartz glass crucibles, (No.1, 6, 8) in Table 2, which were coating treated. The tests were conducted on the following processes. (1) Washing with pure water and drying. (2) Washing with pure water and drying after washing with dilute hydrochloric acid. The adhesion amounts of the residual barium on the surface after each washing test, are shown in Table 3. Regarding the quartz glass crucible of the present invention (No.1), barium was not removed, and the adhesion amounts were not changed in the water washing process (1) and the acid washing process (2). Moreover, regarding the quartz glass crucible of the present invention (No.6), although the form of barium was the barium carbonate, which was same as the conventional one, since the barium carbonate was dispersed in the silica sol liquid and coated and baked, the coated silica became the preservation layer. Thus the barium was not removed in the washing process (1) and the acid washing process (2) like said quartz glass crucible (No.1). On the other hand, regarding the conventional quartz glass crucible (No.8), since the barium carbonate was only adhered on the surface, the barium was washed away a little in the water washing process (1), and the barium carbonate was washed away completely in the acid washing process (2).

[0027]

[EXAMPLE 6]

Test of the dislocation free ratio

The pulling up tests of the silicon single crystal were carried out by using quartz glass crucibles having the transparent coated layer (No.1 to No.5), and the quartz glass crucible, in which the barium carbonate powder was dispersed in the partial hydrolyzate of the alkoxysilane oligomer (No.6). The dislocation free ratio of the pulled crystal (the yield of single crystallization of silicon), are shown in Table 4. Moreover, for the comparison, the same pulling up tests were also conducted on the quartz glass crucible (No.7), in which the surface was not modified and there was no crystallization promoter layer on its surface and on the quartz glass crucible (No.8), in which the crystallization promoter layer was formed by a conventional method. The dislocation free ratio of the single crystal are shown in Table 4. In addition, the thickness of the crystallization layer of the crucible after pulling up the single crystal was measured. The thickness of the crystallization layers is also shown in Table 4. As shown in the results in Table 4, regarding the quartz glass crucible of the present invention, the crystallization layers having the sufficient layer thickness were formed on the surface of the crucible also with comparatively a little amount of barium, and the high dislocation free ratio could be obtained. On the other hand, regarding the quartz glass crucible of the comparative example No.7, the dislocation free ratio was remarkably low. Moreover, regarding the quartz glass crucible (No.8), in which the barium carbonate was adhered by the conventional method, when this quartz glass crucible had the almost same

adhesion amount of barium as used of the present invention, the crystallization layer after pulling up the single crystal was not presented in the crucible, and the dislocation free ratio was remarkably low.

[0028]

[EXAMPLE 7]

Other crystallization promoter

2-ethylhexanoicacid salts of Mg, Ca, and Sr were respectively added to the partial hydrolyzate of alkoxysilane oligomer shown in Table 1 (I) to prepare the silica sol liquids. These silica sol liquids were sprayed to coat each quartz piece having 10 cm square, and the transparent coated layers were formed by baking said coated liquid at 500℃ for 30 minutes. The adhesion amount of the metal, which was calculated as an oxide, were adjusted so that it became 1μg / cm^2. Next, these pieces were put into an electric furnace to bake at 1450℃ for 5 hours in argon gas of 1 atmospheric pressure. Then, it was confirmed that the uniform crystallization layers could be formed by also using all said metals.

[0029]

[Table 1]

	Olygomer (I)	Olygomer (II)
Starting Raw Material and Used Amount	Ethylsilicate40 150g	Ethylsilicate40 67.5g
Solvent and Used Amount	Ethylalcohol 400g	Ethylalcohol 1.1g
Catalyst and Used Amount	60% concentration of Nitric acid 0.6g	60% concentration of Nitric acid 0.7g
Additional Amount of Water	45g	36.4g
Reaction Temperature and Time	45℃ · 3hours	45℃ · 3hours
Silica Solid Part	About 10 wt %	About 25 wt %

[0030]

[Table 2]

No.	Silica Sol Liquid						Adhesion Amounts of Metal Oxide
	Kinds	Olygomer	Solutions Containing Metal Salt	Dilution Alcohol	BaO Amounts	SiO_2 Amounts	
1	A	(Ⅰ) 20g	5 wt % Calculated as BaO 20g	Butanol 60g	1	2	0.6
2	B	(Ⅰ) 20g	5 wt % Calculated as BaO 40g	Butanol 40g	2	2	0.8
3	C	(Ⅰ) 5g	10 wt % Calculated as BaO 50g	-	5	5	0.9
4	D	(Ⅱ) 40g	10 wt % Calculated as BaO 50g	Isoamyl 10g	5	10	5.2
5	E	(Ⅱ) 80g	10 wt % Calculated as BaO 20g	-	2	20	9.5
6	F	(Ⅰ) 100g	Barium Carbonate Powder 0.5g	-	0.4	10	2.1
7	G	Non-Surface Treatment					0
8	H	Conventional Ba Carbonate Powder					0.9

(Note) (Ⅰ) and (Ⅱ) of Olygomers are same as Table 1, Amounts of BaO and SiO_2 is wt %, Isoamyl is Isoamyl Alcohols, Adhesion Amounts of Metal Oxide is μg / cm^2

[0031]

[Table 3]

Sample No.	1	6	8
Silica Sol Liquids	A	F	H
Hardness of Coated Layer (Hardness by Pencil)	No Cracking by 6H	No Cracking by 6H	Cracking given by 6H
Adhered Metal Amount after Washing Non-washing	0.6	2.1	0.9
(1) Amounts After Water Washing and Drying	0.6	2.1	0.8
(2) Amounts After Acid Washing, Water Washing, and Drying	0.6	2.1	0

(Note) Metal amounts is μg / cm^2

[0032]

[Table 4]

No.	1	2	3	4	5	6	7	8
Dislocation free ratio %	73	75	77	76	71	73	35	40
Crystallization Layers After Pulling up μm	80	77	83	95	90	103	0	0

[0033]

[Effect of the Invention]

A quartz glass crucible has a transparent coated layer containing the crystallization promoter on the surface, and since said coated layer forms an integrated structure to the surface of the crucible, there is no abrasion and the adhesion state of a crystallization promoter, such as barium, contained in the coated layer, is kept uniformly. Therefore, cristobalite formation on the surface of the crucible during pulling up the single crystal is completely uniform, and so that an excellent dislocation free ratio can be obtained. Moreover, there is no problem that the coated layer is abraded when contacted with the handling instruments or the persons, in the working process after making the crucible, during from the inspection to the shipment, and the working process in the user side of the crucible. In addition, there is no conventional problem that the fine barium carbonate powder is scattered whenever the case containing the crucible is opened.

[Document Name] Abstract

[Summary]

[Object] A process for modifying the surface of a quartz glass crucible and a surface modified quartz glass crucible produced by the process are provided, wherein the crucible has a transparent coated layer containing a crystallization promoter on the surface.

[Means to be solved] A mixed solution containing a metal organic acid salt and a partial hydrolyzate of alkoxysilane oligomer is coated on the surface of the crucible to be baked to obtain a quartz glass crucible having a transparent coated layer, in which a metal oxide is dispersed in a silica matrix.

[Drawing] No

Historical information of applicant

Identification number : [592176044]

1. Date of change : 21, July, 1992

[Reason] : New registration

Address : 1-5-1, Marunouchi, Chiyoda-ku, Tokyo, Japan

Name : Mitsubishi Material Quartz Co. Ltd.

2. Date of change : 22, May, 2002

[Reason] : Change of company name

Address : 1-5-1, Marunouchi, Chiyoda-ku, Tokyo, Japan

Name : Japan Super Quartz Co. Ltd.